Results in Physics 4 (2014) 105–106

Contents lists available at ScienceDirect

Results in Physics

journal homepage: www.journals.elsevier.com/results-in-physics

Microarticle

Tip-growth of aligned carbon nanotubes on cobalt catalyst supported by alumina using alcohol catalytic chemical vapor deposition

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ARTICLE INFO

Article history:
Received 15 May 2014
Accepted 8 July 2014
Available online 15 July 2014

Keywords:
Aligned carbon nanotube
Tip-growth
Catalytic chemical vapor deposition
Cobalt catalyst
Catalyst support

ABSTRACT

Metal oxide layer helps to support carbon nanotubes (CNTs) aligned perpendicular as well as preventing the tip-growth which takes place due to the strong adhesion force between the catalyst and metal oxide. However, in this work we discovered tip-growth of aligned CNTs with Co as catalyst on thermally oxidized Al/SiO_2/Si substrate system using simple alcohol catalytic chemical vapor deposition technique.

Research on aligned carbon nanotubes (ACNTs) has becoming increasingly popular due to their potential for various applications, e.g. in multiscale devices including energy storage and electronic devices [1–3]. Generally, metal oxide layer (MOL) such as aluminum oxide will lead to the growth of ACNTs due to their surface properties [4]. The porous structure of MOL will "trap" catalyst nanoparticle (CNP) during annealing and produce strong adhesion force due to the obtuse contact angle between them. During CNT growth, MOL will act as a core to support CNT alignment and simultaneously prevent CNP lifts off the substrate during initial hydrocarbon decomposition and carbon diffusion. Therefore, CNT precipitation is compelled to emerge out of metal's apex and carbon crystallizes out as hemispherical dome which then extents up in the form of seamless graphitic cylinder. Subsequent hydrocarbon decomposition takes place on the lower peripheral surface of the metal, and dissolved carbon diffuses upward. Thus CNT grows up with the catalyst particle rooted on its base [5,6]. Recently, by using simple setup of alcohol catalytic chemical vapor deposition technique, we discovered tip-growth of ACNTs on Co/thermally oxidized Al/SiO_2/Si substrate system. After examining the ACNTs with electron microscopes, we observed a formation of amorphous carbon and/or O-ring (ACOr) at the top of some nanotubes; a formation of spherical closed carbon shells which concentric with CNP. This O-r has similarity with nano-onion shape that was able to grow if the CNP size is equal to or more than 50 nm [7].

In our experiment, Al (25 nm) and Co (7–9 nm) thin films were deposited on Si wafer with a 300-nm-thick SiO_2 layer using radio frequency sputtering physical vapor deposition. The substrate was then placed in a furnace at 400 °C (10 min) for Al thermal oxidation process, followed by annealing for 5 min and CNT growth for 10 min at 700–800 °C using ethanol as carbon feedstock. The whole process was done in the same furnace. A field emission scanning electron microscope (FESEM, 20 kV) and a transmission electron microscope (TEM, 120 kV) were used to characterize the morphology of the ACNTs, respectively.

At growth temperature of 750 °C, ACNTs were successfully grown, and during observation, particles with size 10–20 nm were discovered at the top of the ACNTs, which might indicate the presence of Co CNPs (Fig. 1b). The chemical identity of Co CNPs was then confirmed by the energy-dispersive X-ray spectroscopy (EDX) analysis in Fig. 2 by comparing Co content percentage at different spots. The EDX result clearly showed that the brighter spots contain higher percentage of Co as compared to the dark spots which mainly indicated the presence of carbon (the CNTs). Although there is a slight difference in the growth rate, the tip-growth mode is also observable for $T = 700$ and 800 °C samples (Fig. 1a and c).

Meanwhile, TEM image further clarify the presence of Co CNPs inside CNTs which indicated the tip-growth mode (Fig. 3) and the presence of ACOr (Fig. 3, right). In this case, we may assume two ideas; (1) the Co CNP diameter, and (2) the formation of ACOr has driven toward tip-growth mode. The interaction between small carbon patches (small polyaromatic sections or reticulated carbon chains) that were supposed to be built after dehydrogenation of

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http://dx.doi.org/10.1016/j.rinp.2014.07.003
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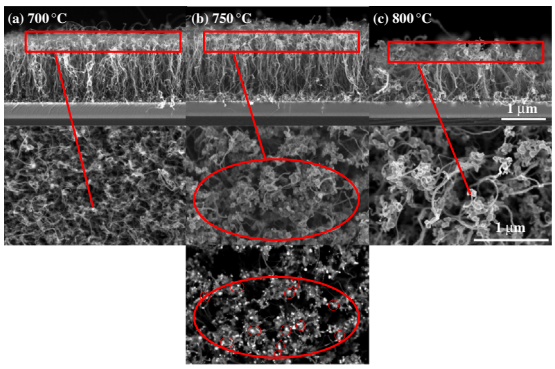

Fig. 1. SEM images (cross section and top view) of ACNT growth at different temperatures (t = 10 min) show small grinds that contain Co CNPs. (b) Backscattered image for almost same spot as top view image was also shown to further indicate the presence of Co CNPs.

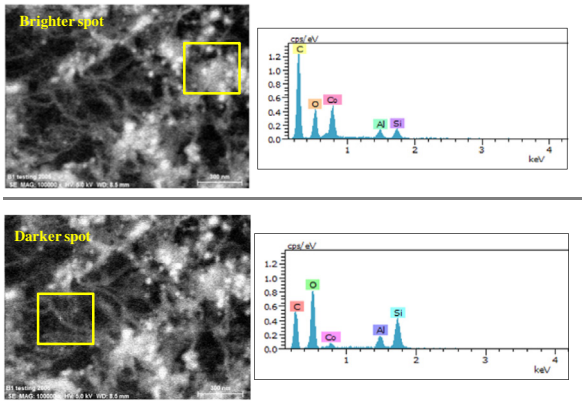

Fig. 2. Comparison of Co catalyst composition at two different spots (bright and dark) by SEM-EDX analysis.

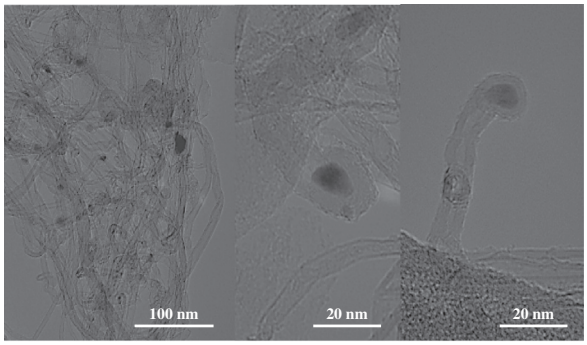

Fig. 3. TEM images of ACNTs. Left image shows bundle of ACNTs with Co CNP at the top and inside the nanotube hollows. Middle and right images indicate the formation of ACOr around Co CNP.

the first carbonaceous molecules and the CNP surface can be considered as the key for tip-growth mode. Therefore, large CNP is less chemically reactive with this carbon patch compared to the smaller one. In terms of kinetics, we can consider that carbon patches have adequate time for diffusion on the surface of large CNP before the formation of complete hemispherical cap. Thus, during CNT nucleation, the first graphitic sections formed on the surface of large CNP diffuse quickly to the catalyst/substrate interface and stabilize it (Fig. 4a). This leaves CNP top surface exposed for further carbon absorption. This nucleation step leads to the particle elongation and finally drives the particle lifts off the substrate to form the tip-growth mode [8]. Meanwhile, the formation of ACOr

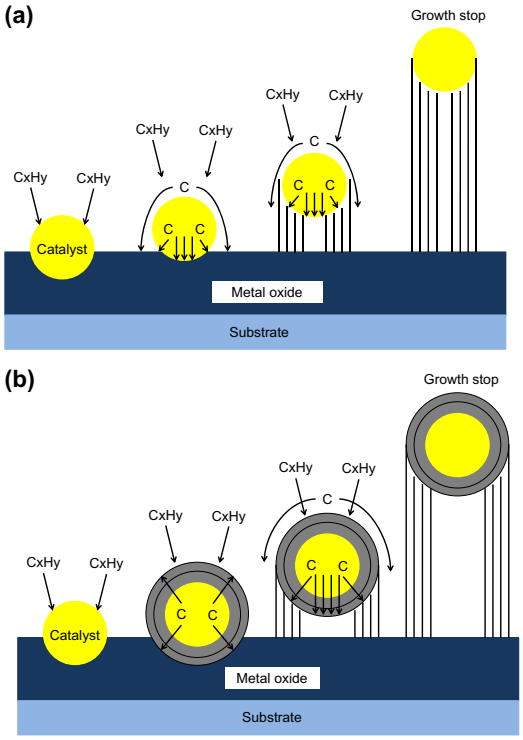

Fig. 4. Our proposed ACNT tip-growth mechanism: (a) large CNP influence and (b) the effect of ACOr formation on tip-growth.

will eventually lift off the Co CNPs from MOL at the early stage of CNT growth. Carbon atom and the graphitic layers were formed around the surface of the solid CNP and then ACOr was attained until the catalytic nanoparticle became poisoned [9]. At this stage the adhesive force between CNP and MOL decreased due to the formation of ACOr. At some point during ACOr formation, the CNPs become saturated due to the carbon solubility limit. Even after ACOr formed, carbon segregation begins which determines the final CNT product (Fig. 4b).

In summary, there is a possibility for tip-growth to occur with the influence of the size of CNPs and formation of ACOr on the CNP surface even with MOL as catalyst support. The cause for ACOr formation might be the same as nano-onion but still needs further investigation.

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